

## Synthesis and Characterization of Surface-Passivated Gold Nanoclusters

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To reveal quantum size effects or non-linear optical responses of gold nanoclusters, we aim at producing gold nanoclusters with well-defined sizes. For the production of the nanoclusters, we have chosen to adopt the method developed by Brust et.al.[1]. This is a liquid-phase production method of gold nanoclusters with surface-passivating thiols, which enables us to produce size-controlled clusters in large quantity. Briefly, an aqueous solution of hydrogen tetrachloroaurate and a solution of tetraoctylammonium bromide in toluene are mixed and stirred so that the tetrachloroaurate is transferred into the organic layer. Dodecanethiol is then added to the separated organic layer, to which an aqueous solution of sodium borohydride is further added to reduce gold ions. This procedure leads to formation of gold nanoclusters with thiol molecules as surfactants.

For analyzing size distributions of produced gold clusters. We use several analyzing techniques such as transmission electron microscope (TEM), optical absorption spectroscopy, and plasma desorption mass spectrometry (PDMS).

TEM observations have shown that gold nanoclusters with diameters around 2nm can be effectively produced with the synthesis method. Fig.1 shows the size distribution of the gold clusters observed by using PDMS. The method involves high-energy (MeV) Si ions from the tandem accelerator of AIST Chubu. Impacts of the heavy energetic ions on the gold nanocluster film desorbes the gold nanoclusters rather intact. The mass distribution of desorbed ions are measured by a time-of-flight technique. As shown in the figure, the desorbed gold clusters have diameters of about 2 nm, which is in good agreement with the TEM observations.

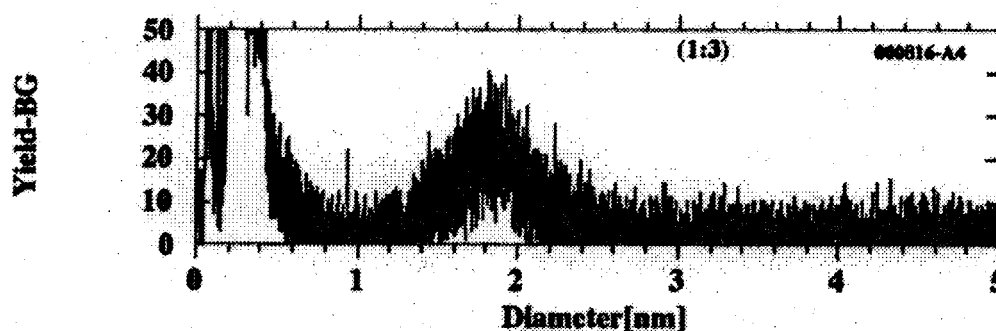


Fig.1 Size distribution of gold nanoclusters measured by using PDMS.

- [1] M.Brust, M.Walker, D.Bethell, D.J.Schffrin and R.Whyman, J. Chem. Soc., Chem. Commun., 801(1994).

©*List of publications and presentations(after last Symposium)*

(1) Publications

- 1) Y. Fujiwara, T. Kawamoto, M. Ichida, S. Fuchi, Y. Nonogaki, A. Nakamura and Y. Takeda: "Er-related luminescence from self-assembled InAs quantum dots doped with Er by organometallic vapor phase epitaxy", *Journal of Luminescence*, Vol.87-89, pp.326-329 (2000).
- 2) Y. Fujiwara, T. Koide and Y. Takeda (Invited): "Luminescence properties of Er,O-codoped GaP grown by organometallic vapor phase epitaxy", E-MRS Spring 2000 Meeting, Symposium K: Rare Earth Doped Semiconductors III, Strasbourg, France, #0294, May 30-June 2 (2000).
- 3) T. Koide, Y. Fujiwara and Y. Takeda: "OMVPE growth and properties of Dy-doped III-V semiconductors", *International Conference on the Physics and Application of Spin-Related Phenomena in Semiconductors*, Sendai, Japan, September 13-15 (2000).
- 4) A. Koizumi, H. Moriya, N. Watanabe, Y. Nonogaki, Y. Fujiwara and Y. Takeda: "Luminescence properties of Er,O-codoped InGaAs/GaAs MQW structures grown by organometallic vapor phase epitaxy", *Proceedings of the 25th International Conference on the Physics of Semiconductors*, Osaka, Japan, pp.1389-1390 (2000).
- 5) T. Yamauchi, Y. Matsuba, Y. Ohyama, M. Tabuchi, and A. Nakamura: "Scanning tunneling microscopy / spectroscopy study of band gap in InAs and InGaAs single quantum dots", *Proceedings of the 25th International Conference on the Physics of Semiconductors*, Osaka, Japan, pp.1371-1372 (2000).
- 6) Y. Fujiwara, H. Ofuchi, M. Tabuchi and Y. Takeda: "Growth condition dependences of optical properties of Er in InP and local structures", *InP and Related Compounds*, Chapter 7, Ed., M. O. Manasreh (Gordon and Breach, Amsterdam, 2000).
- 7) Y. Takeda and M. Tabuchi: "Monolayer scale analysis of heterostructures and interfaces by X-ray CTR scattering and interference", *InP and Related Compounds*, Chapter 10, Ed., M. O. Manasreh (Gordon and Breach, Amsterdam, 2000).
- 8) Y. Hamanaka, J. Kuwabata, A. Nakamura, I. Tanahashi and S. Omi: "Electron energy relaxation dependent on size and matrix in gold nanocrystal-dielectric composites" *Proceedings of International Conference on Ultrafast Phenomena*, pp.401-403 (2000).
- 9) T. Yamauchi, Y. Matsuba, L. Bolotov, M. Taguchi and A. Nakamura: "A correlation between a gap energy and a size of single InAs quantum dots on GaAs(001) studied by scanning tunneling spectroscopy", *Applied Physics Letters* Vol.77, pp.4368-4370 (2000).
- 10) J. Inoue, S. Nonoyama and H. Itoh: "Double resonance mechanism of ferromagnetism and magneto-transport in (Ga-Mn)As", *Physical Review Letters*, Vol.85, pp.4610-4613 (2000).
- 11) Y. Hamanaka, J. Kuwabata, A. Nakamura, I. Tanahashi and S. Omi: "Ultrafast electron relaxation via breathing vibration of gold nanocrystals embedded in a dielectric medium", *Physical Review B*, Vol. 63, pp.104302 (2001).

- 12) T. Yamauchi, Y. Matsuba, Y. Ohyama, M. Tabuchi and A. Nakamura: "Quantum size effects of InAs- and InGaAs-single quantum dots studied by scanning tunneling microscopy/spectroscopy", Japanese Journal of Applied Physics, Vol.40, pp.2069-2072 (2001).
- 13) J. Inoue, S. Nonoyama and H. Itoh: "Ferromagnetism and spin-dependent transport in magnetic semiconductors", Physica E, in press (2001).
- 14) S. Nonoyama and J. Inoue: "Spin-dependent resonant tunneling in magnetic semiconductors", Physica E, in press (2001).
- 15) Y. Fujiwara, T. Koide and Y. Takeda: "Luminescence properties of Er,O-codoped GaP grown by organometallic vapor phase epitaxy", Materials Science and Engineering B, Vol.18, pp.153-156 (2001).
- 16) Y. Morinaga, T. Edahiro, N. Fujimura, T. Ito, T. Koide, Y. Fujiwara and Y. Takeda: "Magnetic properties of Er or Er,O-doped GaAs grown by organometallic vapor phase epitaxy", Physica E10, pp.391-394 (2001).
- 17) J. Yoshikawa, C. Urakawa, H. Ohta, T. Koide, T. Kawamoto, Y. Fujiwara and Y. Takeda: "ESR study of GaAs:Er codoped with oxygen grown by organometallic vapor phase epitaxy", Physica E10, pp.395-398 (2001).
- 18) H. Ohta, C. Urakawa, Y. Nakashima, J. Yoshikawa, T. Koide, T. Kawamoto, Y. Fujiwara and Y. Takeda: "Codoping effects of O<sub>2</sub> into Er-doped InP epitaxial layer grown by OMVPE", Physica E10, pp.399-402 (2001).
- 19) T. Koide, Y. Fujiwara and Y. Takeda: "OMVPE growth and properties of Dy-doped III-V semiconductors", Physica E10, pp.406-410 (2001).
- 20) T. Yamauchi, Y. Ohyama, Y. Matsuba, M. Tabuchi and A. Nakamura: "Observation of quantum size and alloying effects of single InGaAs quantum dots on GaAs(001) by scanning tunneling spectroscopy", Applied Physics Letters Vol. 79 No.15, in press (2001).
- 21) Y. Tai, M. Watanabe, K. Kaneko, S. Tanemura, T. Miki, J. Murakami and K. Tajiri: "Preparation of Gold Cluster / Silica Nanocomposite Aerogel via Spontaneous Wet-gel Formation", Advanced Materials, in press (2001).
- 22) A. Brataas, M. Hirano, J. Inoue, Yu. V. Nazarov and G. E. W. Baure: "Spin accumulation in a quantum cluster resolved in tunnel junction", Japanese Journal of Applied Physics, Vol.40, pp.2329-2335 (2001).

## (2) Presentations

- 1) 浦川知佳, 吉川順子, 太田仁, 小出辰彦, 川本武司, 藤原康文, 竹田美和: 「ESR による酸素共添加 GaAs:Er の電子状態の解析」日本物理学会第 55 回年会, 関西大学, 大阪, 22aK-13, 3 月 22 日(2000).
- 2) 小出辰彦, 磯貝佳孝, 藤原康文, 竹田美和: 「OMVPE 法による III-V 族化合物半導

- 体への Dy 添加」第 47 回応用物理学学術講演会, 青山学院大学, 東京, 28p-ZG-6, 3 月 28 日(2000).
- 3) Y. Hamanaka, J. Kuwabata, A. Nakamura, I. Tanahashi(Matsushita Electric Co. Ltd.), S. Omi(Hoya): "Electron energy relaxation dependent on size and matrix in gold nanocrystal-dielectric composites", International Conference of Ultrafast Phenomena, Charleston, USA, July 9-13 (2000).
  - 4) 小泉 淳, 守屋博光, 渡邊直樹, 野々垣陽一, 藤原康文, 竹田美和:「減圧 OMVPE 法による  $In_xGa_{1-x}As/GaAs$  MQW 構造中への Er, O 共添加と発光特性」, 第 61 回応用物理学学術講演会, 5p-W-10, 北海道工業大学, 札幌市, 9 月 3 日-7 日(2000).
  - 5) 小出辰彦, 磯貝佳孝, 藤原康文, 竹田美和:「OMVPE 法による III-V 族半導体への Dy 添加と光学的特性」, 第 61 回応用物理学学術講演会, 5p-W-11, 北海道工業大学, 札幌市, 9 月 3 日-7 日(2000).
  - 6) J. Inoue, S. Nonoyama and H. Itoh: "Ferromagnetism and spin-dependent transport in magnetic semiconductors", The International Conference on the Physics and application of Spin-Related Phenomena in Semiconductors, Sendai, September 13-15, (2000).
  - 7) S. Nonoyama, J. Inoue: "Spin-dependent resonant tunneling in magnetic semiconductors", The International Conference on the Physics and application of Spin-Related Phenomena in Semiconductors, Sendai September 13-15, (2000).
  - 8) J. Yoshikawa, C. Urakawa, H. Ohta, T. Koide, T. Kawamoto, Y. Fujiwara and Y. Takeda: "ESR study of GaAs:Er codoped with oxygen grown by organometallic vapor phase epitaxy", International Conference on Physics and Applications of Spin-Related Phenomena in Semiconductors, Sendai, Japan, 13-15 September (2000).
  - 9) T. Koide, Y. Isogai, Y. Fujiwara and Y. Takeda: "OMVPE growth and properties of Dy-doped III-V semiconductors", International Conference on Physics and Applications of Spin-Related Phenomena in Semiconductors, Sendai, Japan, 13-15 September (2000).
  - 10) 野々山信二 (山形大), 井上順一郎:「磁性半導体におけるスピン依存共鳴トンネル効果」, 日本物理学会, 新潟大学, 新潟市, 9 月 22-25 日(2000).
  - 11) 井上順一郎, 野々山信二 (山形大), 伊藤博介:「(Ga-Mn)As の強磁性と電気伝導」, 日本物理学会, 新潟大学, 新潟市, 9 月 22-25 日(2000).
  - 12) 吉川順子, 浦川知佳, 大久保晋, 太田仁 (神戸大理), 小出辰彦, 川本武司, 藤原康文, 竹田美和:「ESR による酸素共添加 GaAs:Er の電子状態の解析 II」, 2000 年日本物理学会秋の分科会, 24 pC-8, 新潟大学, 新潟市, 9 月 22-25 日(2000).
  - 13) 溝田武志, 中尾節男, 丹羽博昭, 斉藤和雄, 三木健:「MeV 重イオン衝撃による二次イオン質量分析法を用いたクラスターの質量分析」, 筑波大学加速器センター25 周年記念シンポジウム タンデム加速器による粒子線科学, 筑波大学, つくば市, 12 月 13 日(2000).
  - 14) 山内武志, 大山泰明, 松葉康, 田淵雅夫, 中村新男:「走査トンネル顕微鏡で見た

- GaAs (001) 面上 InAs, InGaAs 量子ドットの量子サイズ効果と合金化」, シリコン材料.デバイス研究会, 北海道大学, 札幌市, 2月28日-3月1日(2001).
- 15) 山内武志, 大山泰明, 日合大輔, 小出辰彦, 磯貝佳孝, 藤原康文, 竹田美和, 中村新男: 「InP(001)面における ErP の成長と表面構造」, 2001年日本物理学会第56回年次大会, 中央大学, 八王子市, 3月27日-30日(2001).
  - 16) 濱中 泰, 福田和宏, 中村新男, 三木 健, 溝田武志, 村上純一: 「表面修飾した金クラスターの電子緩和ダイナミクス」, 2001年日本物理学会第56回年次大会, 中央大学, 八王子市, 3月27日-30日(2001).
  - 17) 吉川順子, 浦川知佳, 大久保晋, 太田仁, 小出辰彦, 川本武司, 藤原康文, 竹田美和: 「ESRによる酸素共添加 GaAs:Er の電子状態の解析 II」 2001年日本物理学会第56回年次大会, 中央大学, 八王子市, 3月27日-30日(2001).
  - 18) 吉川順子, 浦川知佳, 大久保晋, 太田仁 (神戸大理), 小出辰彦, 川本武司, 藤原康文, 竹田美和: 「ESRによる酸素共添加 GaAs:Er の電子状態の解析 III」, 2001年日本物理学会第56回年次大会, 中央大学, 八王子市, 3月27日-30日(2001).
  - 19) 渡邊政夫, 多井豊, 田尻耕治, 三木健, 金子憲治, 種村栄: 「液相法による Au クラスタ作製及びシリカエアロゲルへの担持」, 超微粒子とクラスター懇談会第5回研究会, 名古屋, 6月7日-8日(2001).
  - 20) 溝田武志, 三木健, 中尾節男, 丹羽博昭, 斎藤和雄: 「1.7 MV タンデム加速器を用いた PDMS と金クラスターの質量分布測定」, 第49回質量分析総合討論会, 東京, 6月18日-20日(2001).
  - 21) Y. Fujiwara, T. Koide, S. Jinno, Y. Isogai and Y. Takeda: "Luminescence properties of Dy-doped GaAs grown by organometallic vapor phase epitaxy", 21st International Conference on Defects in Semiconductors (ICDS-21), Giessen, Germany, July 16-20 (2001), PA122.
  - 22) Y. Takeda and M. Tabuchi: "X-ray Characterization of Epitaxial Layers" (Invited), 11th International Summer School on Crystal Growth, July 24-29, Shiga, Japan (2001).
  - 23) Y. Takeda and M. Tabuchi: "X-ray CTR scattering and interference for atomic-scale characterization of semiconductor heterostructures" (Invited), 13th International Conference on Crystal Growth, July 30-August 4, KyotoS, Japan (2001).
  - 24) 磯貝佳孝, 小出辰彦, 神野真吾, 藤原康文, 竹田美和: 「OMVPE 法により作製した Dy,Er 共添加 GaAs 発光特性」第62回応用物理学学術講演会, 愛知工業大学, 豊田市, 13a-P10-16, 9月13日(2001).
  - 25) 吉川順子, 大久保晋, 太田仁, 磯貝佳孝, 小出辰彦, 神野真吾, 藤原康文, 竹田美和: 「ESRによる GaAs:Dy の電子状態の解析」日本物理学会秋の分科会, 徳島文理大学, 徳島市, 17pTG-1, 9月17日(2001).

### (3)Patent applications(total)

- 1)中村 新男, 濱中 泰, 桑畑 順也, 「高速応答の非拡散型熱散逸装置及びその非拡散型熱散逸方法」, 2000年7月24日、特願 2000-202192